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1. Title of the Invention

METHOD FOR MANUFACTURE OF
ULTRATHIN COPPER FOIL

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Specification

1. Title of the Invention

METHOD FOR MANUFACTURE OF ULTRATHIN COPPER FOIL

2. Patent Claims

A method for the manufacture of an ultrathin copper foil by conducting zinc substitution plating on the edge portion of one surface of an aluminum foil or aluminum alloy foil, then conducting copper plating to a thickness of 0.5-12 μm in a copper pyrophosphate plating bath on

the entire surface of said surface, and then conducting copper plating to a thickness of 8-12 μm in a copper sulfate-based copper plating bath on the outside thereof.

3. Detailed Description of the Invention

The present invention relates to a method for the manufacture of an ultrathin copper foil for high-density printed circuit boards in which a wiring width and wire spacing are greatly decreased.

In recent years, significant progress in electronics technology created a demand for highly reliable high-density printed circuit boards. In particular, in the copper-clad laminates for printed circuits of computers, it became necessary to form ultrafine circuits with a wiring width and wiring spacing of no more than 0.2 mm. However, the thickness of the conventionally used copper foils was as large as about 85 μm . Therefore, in the etching technology at the time, when circuits were formed from such copper foil-clad laminates, there was a danger that the copper foils would be undercut by side etching (a lower side portion of a groove is etched on the periphery thereof and a recess-like portion is obtained), causing a short circuit. For this reason, circuits with high-density wiring widths and wiring spacing could not be obtained. Therefore, it was impossible to obtain highly reliable printed circuits with a high density.

Accordingly, thin copper foils with a thickness of 18-25 μm were used to attain this object. However, since they were manufactured by electrolytic methods similar to those for the manufacture of the above-mentioned thick copper foils, pinholes easily occurred. Moreover, because the foils were so thin, "wrinkles" and "scratches" could easily occur when the foils were handled. A low production yield and a high cost were other drawbacks associated with such ultrathin foils. Furthermore, when such copper foils were employed for forming high-density circuits by a photoresist method, the lower limit for the wiring width and wiring spacing was 0.2 mm, and high-density circuits with an ultrafine pattern having wiring widths and spacing less than this limit were difficult to produce.

An improved method was suggested, this method using an ultrathin copper foil formed by employing an aluminum foil, etc. as a pseudo-substrate and electroplating a copper layer with a thickness of no more than 18 μm thereupon. A glass-epoxy base material was laminated on the copper foil surface, the aluminum foil serving as a pseudo-substrate was removed by chemical or mechanical peeling method, and the resulting copper foil laminated sheet was used to form a high-density circuit by the aforesaid photoresist process. Such a method is disclosed, for example, in Japanese Patent Application Laid-open 48-85857.

However, with such a method, it is necessary to conduct zinc substitution plating on the electrocoating surface of the aluminum foil in advance in order to provide for good bonding strength of the ultrathin copper layer formed by electroplating with the aluminum foil serving as a pseudo-substrate and it was also necessary to dissolve and remove the aluminum and zinc chemically in order to obtain a copper clad laminate after lamination of the glass-epoxy base material. Therefore, in addition to those two types being complicated and wastewater treatment being difficult, there are disadvantages in that the copper layer is partially dissolved when the zinc is removed, and circuit shorts occur easily.

With another suggested method, copper cyanide plating is conducted on one surface of the aluminum foil of the pre-degreased and activated pseudo-substrate. However, in such a case, the copper adhesion strength is insufficient. For this reason, when in subsequent processes a thick copper plating was conducted with an acidic copper plating bath and then treatment was

conducted to increase the adhesive force, the copper layer could be easily peeled off and removed from the surface of aluminum foil. Moreover, when the thickness of the copper plating was less than 12 μm , a large number of fine pinholes were present and the product was not suitable for practical use.

The inventors have conducted an intensive study aimed at the resolution of the above-described problems. Based on the results obtained, a method was developed for the manufacture of an ultrathin copper foil designed for the formation of highly reliable printed circuits with a high density. Thus, with the method in accordance with the present invention zinc substitution plating is conducted on the edge portion on one surface of an aluminum or aluminum alloy foil (referred to simply as aluminum foil hereinbelow), then copper plating is conducted to a thickness of 0.5-12 μm in a copper pyrophosphate plating bath on the entirety of that one surface, and then copper plating is conducted to a thickness of 8-12 μm in a copper sulfate-based copper plating bath on the outside thereof.

The method in accordance with the present invention will be described hereinbelow in greater detail.

At least one surface of an aluminum foil with a thickness of 30-70 μm (a long foil with a width of 300-1300 mm) is degreased with an alkaline cleaner and washed with water according to the usual procedure. If necessary, washing with water is conducted after pickling with 50% HNO_3 or activation.

Then an edge portion on one surface of the foil is immersed for 2-120 sec in the so-called zincate bath and zinc substitution plating is conducted. In this case, the edge portion as referred to hereinabove is a frame-like portion located on the periphery of the aluminum foil; it has a width of 2-100 mm, preferably, 10-50 mm. This width is referred to as an edge width.

The zinc substitution plating is conducted to improve adhesion of copper layer to the aluminum foil in the portions that are directly subjected to copper plating. Thus, when the end portion of the aluminum foil is not subjected to zinc substitution plating, a copper pyrophosphate plating itself cannot provide for a sufficient bonding strength with the surface of aluminum foil. When, in such a state, water washing and copper sulfate thick plating are performed in the subsequent process, the copper layer can easily peel from the edge portion of the aluminum foil. Moreover, if the coating peels off even slightly, then water or plating solution rapidly penetrates into the interface between the aluminum foil and copper layer, the surface of aluminum foil is corroded mainly by the plating solution, and the peeling is further promoted. Even if the substrates in such a state are finally dried, since the major portion of the copper layer has peeled from the pseudo-substrate, "wrinkles" or a large number of pinholes appear therein, making the foil unsuitable for practical use. However, if zinc substitution plating of the edge portion of aluminum foil is conducted as described above, the bonding strength with respect to the copper pyrophosphate plating bath is also improved and no peeling occurs in subsequent plating in a copper sulfate bath. Moreover, when the copper plating is formed to a thickness of no less than 5 μm , practically no pinholes are formed.

Immediately after completion of the zinc substitution plating, a copper layer with a thickness of 0.5-12 μm is plated by using a copper pyrophosphate plating bath, followed by washing with water. In such a case, no specific limitation is placed on the composition of the copper pyrophosphate plating bath, but it is preferred that the copper concentration be 5-100 g/L, the concentration of potassium pyrophosphate be 100-500 g/L, and the pH be 8-12. As for the plating conditions, the bath temperature is within a range from normal temperature to 70°C, the electric current density is 1-5 A/dm^2 , and the electrolysis time is 5-25 sec.

The copper pyrophosphate plating bath is selected for the purposes of the present invention because the coating obtained with such a bath has better adhesion to aluminum foils than that obtained with other copper plating baths, and, naturally, no peeling occurs in the lamination of laminated base materials for printed circuits. Furthermore, in addition to that fact that stronger adhesion cannot be maintained, it is not necessary to chemically dissolve and remove the aluminum foil pseudo-substrate after lamination of the base material, and peeling can be conducted by a simple mechanical means. As a result, wastewater treatment is made unnecessary, and the aluminum used can be easily recovered in the form of aluminum chips. Furthermore, a copper pyrophosphate plating bath makes it possible to conduct uniform electrocoating, and a coating can be obtained which is smooth and has good gloss. Moreover, a very small number of pinholes appear even when a thin copper foil is obtained. The thickness of the copper pyrophosphate plating is limited to 0.5-1.2 μm for the following reasons. When the thickness is less than 0.5 μm , the number of pinholes in a thin copper foil obtained increases, making it unsuitable for practical use. On the other hand, when the thickness exceeds 12 μm , since the upper limit of thickness of thin copper foils is 15 μm , the copper sulfate plating in the subsequent process cannot be conducted. Moreover, adhesion to plastic laminated base materials is degraded. The thickness of the copper foil layer is preferably 2-7 μm .

Plating copper to a thickness of 8-12 μm in a copper plating bath containing copper sulfate is conducted as a method for roughening of the copper foil layer. Appropriate conditions of such treatment should be selected and no specific limitation is placed thereon. Typically the copper plating bath has a copper concentration of 20-60 g/L and a sulfuric acid concentration of 40-150 g/L. The bath temperature is preferably within a range from normal temperature to 60°C. As for the electric current density and electrolysis time, they are somewhat affected on the liquid flow parameters, stirring state, and plating thickness, but preferably they are usually within the ranges of 5-40 A/dm² and 1-10 min, respectively. The external appearance of the obtained copper plated film must be such that velvety peaks and valleys of red color are formed.

The thickness of the copper plated layer is limited to 8-12 μm for the reasons as follows. The entire thickness of plated copper layer may be 15 μm and the thickness of the plated layer obtained by using a copper sulfate bath may be adjusted by varying the thickness of the plated layer obtained with the above-mentioned copper pyrophosphate plating bath.

The plated layer with the above-mentioned roughening treatment is further laminated with a plurality of layers of a composition prepared by infiltrating an insulating substance such as glass fibers with an epoxy resin, and then the aluminum foil pseudo-substrate is peeled off, thereby obtaining a final product.

In this case, the bonding strength between the plated copper layer subjected to the roughening treatment and said laminated insulating material may be about 1.6-1.8 kg/cm², but if it is less than 1.6 kg/cm², secondary roughening treatment copper plating is conducted on the outer side of the copper plated layer. For this purpose a method can be used in which, for example, cathodization is conducted at a current density of 2-20 A/dm² for 2-120 seconds in an acidic copper electrolytic bath having added therein ions of at least one metal selected from a group including arsenic, antimony, and bismuth.

Embodiments of the present invention will be described hereinbelow

Embodiment 1

A soft pure aluminum foil (99.9%) with a thickness of 70 μm was degreased by immersion for 3 min in a solution of sodium orthosilicate (100 g/L) at a temperature of 70°C, and then pickling and activation treatment was conducted by immersion for 1 min at a temperature of 25°C in an aqueous solution of HNO_3 with a concentration of 350 g/L. Then, an edge portion (edge width 20 mm) on only one side of the aluminum foil was selectively subjected to local zinc substitution plating by immersion for 60 sec in a solution (liquid temperature, room temperature) consisting of ZnO 30 g/L and NaOH 100 g/L. Then, one side of the aluminum foil was plated with copper for 5 min at an electric current density of 2 A/dm^2 in a plating bath (liquid temperature 50°C) having a Cu concentration of 30 g/L and a potassium pyrophosphate concentration of 150 g/L and a pH of 8.8. Finally, the plated layer was subjected to roughening copper plating for 2 min at a current density of 10 A/dm^2 in a plating bath (liquid temperature 20°C) containing Cu at 20 g/L and H_2SO_4 at 75 g/L. As a result, an ultrathin copper foil with a copper layer thickness of 6 μm was obtained.

Embodiment 2

A hard aluminum alloy foil (Al 99.7%, Cu 0.05%, Fe 0.05%, Si 0.20%) with a thickness of 30 μm was subjected to degreasing by immersion for 30 sec at a temperature of 50°C in a solution containing sodium orthosilicate 100 g/L, NaOH 30 g/L, and nonionic surfactant 0.1 g/L. Then, pickling and activation treatment was conducted by immersion for 30 sec at a temperature of 25°C in a solution consisting of HCl 100 g/L and NaCl 50 g/L. Then, local zinc substitution plating was conducted selectively only on the edge portion (edge thickness 35 mm) on one side of the aluminum alloy foil by immersion for 38 sec in a solution (liquid temperature, room temperature) consisting of ZnO 5.0 g/L, NaOH 200 g/L, and FeCl_3 5 g/L. One surface of the aluminum foil was then plated with copper for 10 min at a current density of 3 A/dm^2 in a plating bath (liquid temperature 60°C) consisting of Cu 80 g/L and potassium pyrophosphate 30 g/L, and having a pH of 9.3. Then roughening copper plating of said plating layer was conducted for 60 sec at a current density of 6 A/dm^2 in a plating bath (liquid temperature 25°C) consisting of Cu at 30 g/L and H_2SO_4 at 100 g/L. Finally, the resulting roughened plated layer was subjected to secondary roughening copper plating for 20 sec at a current density of 6 A/dm^2 in a solution consisting of Cu $(\text{BF}_4)_2$ 25 g/L, HBF_4 42 g/L, $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ 0.9 g/L (liquid temperature 12°C), and an ultra thin copper foil with a copper layer thickness of 7 μm was obtained.

Embodiment 3

A hard aluminum alloy foil (Al 99.3%, Cu 0.04%, Fe 0.07%, Si 0.15%, Zn 0.05%, Mg 0.10%, Ti 0.05%) with a thickness of 50 μm was subjected to anodic electrolytic degreasing for 30 sec at a current density of 2 A/dm^2 in a solution containing sodium orthosilicate 100 g/L, NaOH 30 g/L, and a nonionic surfactant 0.1 g/L. Then only the edge portion (edge width 15 mm) of the Al alloy foil was selectively subjected to local zinc substitution plating by treating for 20 sec in a solution (liquid temperature 30°C) consisting of ZnO 70 g/L and NaOH 400 g/L. Then, one surface of the aluminum foil was plated with copper for 15 minutes at a current density of 3 A/dm^2 in a plating bath (liquid temperature 60°C) having a Cu concentration of 100 g/L, a potassium pyrophosphate concentration of 250 g/L, and a pH of 9.0. Then, the copper plated

layer was subjected to roughening copper plating for 75 sec at a current density of 32 A/dm^2 in a plating bath (liquid temperature 65°C) having a Cu concentration of 50 g/L and an H_2SO_4 concentration of 50 g/L. Finally, the roughened copper plated layer was subjected to secondary roughening copper plating for 32 sec at an electric current density of 4 A/dm^2 in a solution (liquid temperature 15°C) containing Cu at 7 g/L, H_2SO_4 at 32 g/L, H_3AsO_4 at 0.4 g/L, and H_2SiO_3 at 0.2 g/L, and an ultrathin copper foil with a copper layer thickness of $5 \mu\text{m}$ was obtained.

Comparative Example 1

A hard aluminum alloy foil (Al 99.7%, Cu 0.5%, Fe 0.05%, Si 0.20%) with a thickness of $30 \mu\text{m}$ was subjected to degreasing by immersion for 3 min in a solution (liquid temperature 70°C) consisting of sodium carbonate 30 g/L and sodium phosphate 50 g/L, and then an edge portion of 15 mm on one surface of the aluminum alloy foil was selectively subjected to zinc substitution plating by immersion for 20 sec in a solution containing ZnO at 70 g/L and NaOH at 400 g/L (liquid temperature 30°C). Then, copper plating was performed on the entirety of one surface of the aluminum alloy foil for 15 minutes at an electric current density of 3 A/dm^2 in a plating bath (liquid temperature 40°C) having a Cu concentration of 100 g/L, a potassium pyrophosphate concentration of 250 g/L, and a pH of 9.0, then the copper plated layer was subjected to roughening copper plating for 75 sec at an electric current density of 32 A/dm^2 in a plating bath (liquid temperature 65°C) having a Cu concentration of 50 g/L and an H_2SO_4 concentration of 50 g/L. Finally, the roughened copper plated layer was subjected to secondary roughening copper plating for 32 sec at an electric current density of 4 A/dm^2 in a solution (liquid temperature 15°C) containing Cu at 7 g/L, H_2SO_4 at 32 g/L, H_3AsO_4 at 0.4 g/L, and H_2SiO_3 at 0.2 g/L, and an ultrathin copper foil with a copper layer thickness of $5 \mu\text{m}$ was obtained.

Comparative Example 2

An aluminum alloy foil identical to that of Comparative Example 1 was used and degreasing was conducted in the same manner as in Comparative Example 1. Then, copper plating similar to that of Comparative Example 1 was conducted immediately without zinc substitution plating and thereafter roughening copper plating was conducted to obtain an ultrathin copper foil with a copper layer thickness of $5 \mu\text{m}$.

The ultrathin copper foils with pseudo-substrates attached thereto, which were obtained in the Embodiments 1-3 and Comparative Examples 1-2 were laminated on base materials infiltrated with glass epoxy and then pressing was conducted for 60 min at a pressure of 25 kg/cm^2 and a heating temperature of 160°C to obtain a laminated sheet with a thickness of 2 mm. Copper-clad laminated sheets were then obtained by mechanically peeling off the pseudo-substrates of aluminum foils, copper pyrophosphate plating was thereafter conducted to increase the thickness of the copper layer to $15 \mu\text{m}$, and the bonding strength and pinholes were measured by the usual method. The results are presented in Table 1.

The bonding strength was measured by applying a peeling force in the direction of 90° to a width of 10 mm. The number of pinholes was counted by illuminating the layer from below a dark room and observing the transmitted light.

Table 1.

	Number of pinholes (holes/m ²)	Bonding strength (kg/cm ²)	External appearance of copper foil
Embodiment 1	2-4	1.6-1.7	Fine velvety peaks and valleys
Embodiment 2	1-2	2.0-2.4	"
Embodiment 3	0	2.0-2.4	"
Comparative Example 1	20-100	1.5-1.7	Bulbous peaks and valleys
Comparative Example 2	Very large number	1.4-1.8	"

As follows from the table presented above, the ultrathin copper foils obtained by the method in accordance with the present invention have a number of pinholes substantially less than that in the ultrathin foils obtained by the conventional methods and also have excellent bonding strength.

Patent Representative. Patent Attorney: Takehiko Suzue.

5. List of Appended Items

(1) Power of attorney	2 copies
(2) Specification	1 copy
(3) Drawings	1 copy 1 [illegible]
(3) (4) Copy of application	1 copy 3 [illegible]

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印パターンを有する蒸気凝縮膜の外成は逆置で
もつた。

又この成膜方法としてアルミニウム箔を成
膜体とし、その上に電気メッキ法により厚さ 10
μm 以下の腐食性無メッキを形成せしめた成膜体
を用い、成膜体表面にガラスエポキシ高粘着
剤を塗布した後、成膜体のアルミニウム箔を化学
的又は物理的剥離法により剥離し、無膜を
剥離とし、これを前記のフォトリソ法により
露光成膜膜を形成せしめる方法が特許文
明第 8-83883 号公報に記載されている。

然しながらこの方法は電気メッキにより成
膜される無膜体成膜体のアルミニウム箔とを、
よく剥離せしめるために予めアルミニウム箔
の表面を粗面を形成するメッキとしておく必要がある
とされガラスエポキシ高粘着剤を塗布後、無膜
を剥離するための化学的又は物理的剥離法により
剥離せしめなければならぬ。従つて
この方法が有難であり且つ露光成膜膜が粗面
であると剥離が容易であるが一部無膜を剥離

のメッキを行うものである。

本発明方法について以下詳細に説明する。

30～70μm のアルミニウム箔（厚さ 300～
1300mm の長尺箔体）の少なくとも片面を常法
のアルカリソーダ水により脱脂し水洗する。
なおこの場合必要により 50 多 HNO₃ 等で酸洗し
しくは活性化した後水洗する。

次いで箔体の片面の表面を所定レンジで
研磨し 2～120 秒浸漬して、表面粗度メッキ
を施す。なおこの場合粗度とはアルミニウム箔
の表面に設けた突起の高さをいい、その巾は 2～
100μm、高さしくは 10～50μm である。こ
の巾を線粗巾という。

而して表面粗度メッキを施す理由は表面粗度メ
ッキされる部分のアルミニウム箔に対する腐蝕
の増進を向上せしめるためである。即ちアル
ミニウム箔の表面に表面粗度メッキを施さない
場合にはビロリン酸メッキ溶液自体アルミニウム
箔面に対して十分に腐蝕性を保持し得ないため
であり、このような状態において水洗後には表

面粗度 52-16433 の
され、表面粗度を生じない欠点がある。

又粗度メッキとして予め粗度、活性化した後
成膜アルミニウム箔の片面にビロリン酸メッキ
溶液より表面粗度メッキを行うこともあるが、
この場合粗度の粗度度が十分でないため、その後
の工程において、表面粗度メッキより粗度内
メッキを行い、更に粗度力の向上処理を行う際
に、表面粗度がアルミニウム箔表面から剥離、破
壊し易く且つ表面メッキの厚さが 12μm 以下の
範囲には粗度の粗度をピンホールが形成し表面
上作用し得ないものである。

本発明はかかる欠点を改善するため表面粗度
を行うため、表面粗度として、・表面粗度のプリ
ントを施すため、表面粗度の粗度力
は生じ出したものである。即ち本発明はアル
ミニウム箔又はアルミニウム箔（以下アル
ミニウム箔という）の片面に表面粗度メッキ
メッキを行つた後、箔片面全面にビロリン酸メ
ッキ溶液で 0.5～12μm の粗度メッキを行い、更
にその外側に表面粗度メッキ溶液で 8～12μm

工程における表面粗度メッキを施す際に、
アルミニウム箔の表面から粗度が剥離するの
ならず一旦少しでも粗度があると表面粗度メ
ッキ溶液がアルミニウム箔と粗度との界面に浸透
し、表面粗度メッキより主としてアルミニウム箔
の表面を腐食しつづつ表面粗度を剥離する。この
ような状態のものを表面粗度には剥離するとして
も粗度の大部分が表面粗度から剥離しているため
「しわ」または粗度のピンホールを生じ粗度
は生じないものとなる。しかし表面粗度の粗度アル
ミニウム箔の表面に表面粗度メッキを施すこと
よりビロリン酸メッキ溶液に対する粗度性も良
好であり且つその後の表面粗度メッキ溶液中に
かかる粗度もかからないとされる。以上の粗度
メッキを形成せしめた場合ピンホールは殆んど見
られないものとなる。

而して表面粗度メッキを施した表面粗度メ
ッキ溶液メッキ溶液より 0.5～12μm の粗度メ
ッキを行ない水洗する。この場合ビロリン酸メ
ッキ溶液の粗度については別に決定するものではな

は、大きくは数分～100分/平方メートル、カリウム100～500g/m²、石灰もこのくらい。又ノリ鉄分については数分～70分、硫酸酸度1～5A/dm²、有機物分は8～9分におよび行くものである。

又本発明においてはピロリン酸カルシウムを起
点とする肉付け用の材料とを比較してアルミニウ
ム塩に対する電着性が比較的良形であり、プ
リントの印刷用紙を容易に積層せしめる際において
自然に調整のトラブルをおこすことがない。且
て強固な密着性を確保し得ることと並行して、
積層膜を剥離性、アルミニウム塩の電着性を化
学的に制御して除去する必要な厚膜形成作
業のみで剥離させることが出来るため、印刷の
処理も必せず、厚膜アルミニウム層としてそ
のままで収めることが出来る。更にピロリン酸
カルシウム等は電着を効に行うことが出来るた
め、平滑にして光沢を有する層とが可能であ
り、無垢銅板とした場合においてもピンホール
が極めて少ない。又ピロリン酸カルシウムの電着を

各材料の厚みを5〜12mmに所
 し、先由は合鋼の厚みが5mmに
 ばよく、前記のピロリン鋼の厚
 みを5mmにばよく、前記のピロ
 リン鋼の厚みを5mmにばよく、

次いで新記固晶化を為すメツケ脂の上で、無
性物質を加へガラス融液状エポキシ樹脂を充
したものを冷却板に押し入れ、アルミニウム箔
の製成体を糊として封鎖化するものである。

なおこの場合凹凸化処理の銅メッキ膜と被膜の乾燥温度と凹陥の深さが $1.6 \sim 1.8 \text{ kg/cm}^2$ 程度であればよいが、 1.0 kg/cm^2 未満の圧力では、銅メッキ膜の外側に凹凸化処理の銅メッキを行ってもよい。その方法としては銅メッキ液アンチモン、ヒスマスの1層又は2層以上の塗布イオンを $0.0001 \sim 0.05 \text{ mol/l}$ の濃度にした溶液を溶液中において電流密度 $2 \sim 5 \text{ OA/dm}^2$ 、 $2 \sim 10$ 秒間処理処理を行ってもよい。

次に本邦の興業について説明する。

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0.5 ~ 1.2 mm 程度にしたものは 0.5 mm 程度の厚さには作られただけで、治具のピンホールが多く、また表面に凹凸し、硬いものとなり、1.2 mm を加えた場合は伸縮性弱く、としての伸びが 1.5 mm であるため、各工程の伸縮率を 1.2 mm を行うことができなくなり、且つプラスチックの成形材料との密着性にも悪いためである。なお、0.5 mm の厚みは、厚くしくは 0.8 ~ 1 mm が良い。

ばいて上製鋼溶融の上で四凸化処理粉として
 鋼が軟化し、ノヤ当にて8~12μの鋼メッキ
 を施す。その良好性については調査報告すべきで
 あり、これに限定する金銭はないが、一般に鋼板
 メッキの場合の相場として、鋼板厚20~30
 g/m²、処理時間40~150分、鋼板を常温
 ~80℃にすることが望ましい。又、電流密度
 を知る制についてはおのれ、隆昇状況、メ
 ック厚より一般には不足ないが通常5~40
 A/dm²、1~10分が望ましい。かくして、鋼
 メッキの外装は緑色のビロード状凹凸のも
 のを形成することが必要である。

70%の軟質銅アルミニウム箔(99.9%)をオムトキイ酸ナトリウム100g/gの溶液中に70℃で3分間浸漬して処理を行い、次いで350g/g HNO₃水溶液中に25℃において1分間浸漬して酸洗並活性化処理を行う。該アルミニウム箔の片面総重(標準厚20μ)のみを基的にZn30g/g、NaOH100g/gからなる溶液(微品、塩酸)中に60秒間浸漬せしめ部分亜鉛置换メッキを行う。次いで該アルミニウム箔の片面をCu濃度30g/g、ピロリン酸カリウム250g/g、H₂Oからなるメッキ液(微品50℃)中に置いて、電流密度2A/dm²により5分間銅メッキを行い、最後に該メッキ層をCu濃度20g/g、H₂BO₃75g/gからなるメッキ液(微品20℃)中に置いて、電流密度10A/dm²により3分間凹凸化銅メッキを行つて銅厚厚6μの複層銅箔を得た。

實施例 2

90 度硬質アルミニウム合金板 (4499.7 号、

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Cu 0.05 g, Fe 0.05 g, Bi 0.20 g) をアルトケイ酸ナトリウム 100 g/g, NaOH 30 g/g, ノニオン系界面活性剤 0.1 g/g からなる溶液中に 50℃ において 30 秒浸漬して脱脂を行い、次いで HCl 100 g/g, NaCl 50 g/g からなる溶液中に 25℃ において 30 秒浸漬して腐食処理に付した後、該アルミニウム合金箔の片面面積 (露出部 3.5 cm²) のみを選択的に Zn 0.50 g/g, NaOH 200 g/g, FeCl₂ 5 g/g からなる溶液 (液温、室温) 中に 30 秒間浸漬せしめ部分亜鉛鍍メツヤを行つた後、次いで該アルミニウム箔の片面を Cu 80 g/g, ピロリン酸カリウム 30 g/g, pH 9.3 からなるメツヤ液 (液温 60℃) 中に 10 分間、電流密度 8 A/dm² により銅メツヤを行い、次いで該メツヤ層を Cu 鍍層 30 g/g, H₂SO₄ 100 g/g からなるメツヤ液 (液温 25℃) 中に 60 秒間、電流密度 6 A/dm² により凹凸化銅メツヤを行い、最後に該凹凸化メツヤ層の上に Cu(BF₄)₂ 25 g/g, HBF₄ 42 g/g,

Na₂AuCl₄·12H₂O 0.9 g/g からなる溶液 (液温 12℃) 中に 20 秒間、電流密度 6 A/dm² にて 2 次凹凸化銅メツヤを行つて銅箔厚 7 μm の極薄銅箔を得た。

比較例 3

50 μm の厚さアルミニウム合金箔 (AL99.3 g, Cu 0.04 g, Fe 0.07 g, Bi 0.15 g, Zn 0.03 g, Mg 0.10 g, Ti 0.05 g) をアルトケイ酸ナトリウム 100 g/g, NaOH 30 g/g, ノニオン系界面活性剤 0.1 g/g からなる溶液中に 30 秒間電流密度 2 A/dm² により防錆電解処理を行い、次いで該 AL 合金箔の端面 (露出部 1.5 cm²) のみを選択的に Zn 0.70 g/g, NaOH 400 g/g からなる溶液 (液温 30℃) 中に 20 秒間浸漬せしめて部分亜鉛鍍メツヤを行つた後、次いで該アルミニウム箔の片面を Cu 鍍層 100 g/g, ピロリン酸カリウム 250 g/g, pH 9.0 からなるメツヤ液 (液温 60℃) 中に 15 分間、電流密度 3 A/dm² にて銅メツヤを行い、次いで該銅メツヤ層

を Cu 鍍層 50 g/g, H₂SO₄ 50 g/g からなるメツヤ液 (液温 65℃) 中に 75 秒間、電流密度 32 A/dm² にて凹凸化銅メツヤを行い、最後に該凹凸化銅メツヤ層の上に Cu 鍍層 7 g/g, H₂SO₄ 32 g/g, H₂AsO₄ 0.4 g/g, H₂SiO₃ 0.2 g/g からなる溶液 (液温 15℃) 中に 32 秒間、電流密度 4 A/dm² にて 2 次凹凸化銅メツヤを行つて銅箔厚 1.5 μm の極薄銅箔を得た。

比較例 1

30 μm の厚さアルミニウム合金箔 (AL99.7 g, Cu 0.5 g, Fe 0.05 g, Bi 0.30 g) を炭酸ソーダ 30 g/g, リン酸ソーダ 50 g/g からなる溶液 (液温 70℃) 中に 3 分間浸漬して脱脂を行い、次いで該アルミニウム合金箔の片面面積 1.5 cm² を選択的に Zn 0.70 g/g, NaOH 400 g/g からなる溶液 (液温 30℃) 中に 20 秒間浸漬して部分亜鉛鍍メツヤを行い、次いで該アルミニウム合金箔の片面の全面に Cu 鍍層 100 g/g, ピロリン酸カリウム 250 g/g,

pH 9.0 からなるメツヤ液 (液温 40℃) 中に 15 分間、電流密度 3 A/dm² にて銅メツヤを行い、次いで該メツヤ層の上に Cu 鍍層 50 g/g, H₂SO₄ 50 g/g からなるメツヤ液 (液温 65℃) 中に 75 秒間、電流密度 32 A/dm² にて凹凸化銅メツヤを行い、最後に該凹凸化銅メツヤ層の上に Cu 鍍層 7 g/g, H₂SO₄ 32 g/g, H₂AsO₄ 0.4 g/g, H₂SiO₃ 0.2 g/g からなる溶液 (液温 15℃) 中に 32 秒間、電流密度 4 A/dm² にて 2 次凹凸化銅メツヤを行つて銅箔厚 5 μm の極薄銅箔を得た。

比較例 2

比較例 1 と同様のアルミニウム合金箔を使用し、比較例 1 と同様に脱脂処理を行つた後亜鉛鍍メツヤを行ふことなく、直ちに比較例 1 と同様の銅メツヤを行い更に凹凸化銅メツヤを行つて銅箔厚 5 μm の極薄銅箔を得た。

而して上記実施例 1～3 及び比較例 1～2 より得た低基板付極薄銅箔をガラスエポキシ含浸基板の上に置いた後、加熱温度 150℃、圧

力 2.5 kg/cm^2 において 60 分間加圧して、厚さ 2 mm の積層板とした後、アルキド樹脂系の接着剤と機械的に引き剥して剝貼積層板とした後、銅箔の厚さを $1.5 \mu\text{m}$ にするため、更にポリリン酸銅メッキを行い、常法により接着力並にピンホールを低減した。その結果は図 1 に示す通りである。

なお、接着力は 10 mm につき 90° 方向の引き剥し力によるものであり、ピンホールは場所において下方向から光を当て透過する穴の数をカウントした。

図 1 例

	ピンホール数 (個/ m^2)	接着力 (kg/cm^2)	銅箔の外観
電鍍銅 1	2~4	1.6~1.7	銀線ビロード状凹凸
2	1~2	2.0~2.4	“
3	0	2.0~2.4	“
比較例 1	20~100	1.5~1.7	ランゴ状凹凸
2	無数	1.4~1.8	“

上表より明らかなく本発明方法により得た積

層銅箔は従来方法により得た積層銅箔に比してピンホールが著しく少く且つ接着力において優れたものを得る効果著しい効果を得る。

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5. 給付取得の経緯

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